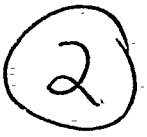

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STRUCTURE OF THE Si_{45} CLUSTER

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ABSTRACT

Six structures for the Si_{45} cluster are compared using a tight-binding model. Two new structures are proposed which appear to be the low-energy isomers and to explain much of the existing experimental data. Cluster reactivity is distinguished from cluster stability, and several reasons are discussed which may lead to a reactive or unreactive species. These criteria are applied to the Si_{45} isomers, and the results are also correlated with experimental data.

I. INTRODUCTION

There has been much interest in the Si_{45} cluster, both from an experimental and theoretical point of view. The original impetus to this effort was the astounding experimental results compiled by Elkind et al,[1] which reported a reactivity difference between various silicon clusters spanning two orders of magnitude. Si_{33}^+, Si_{39}^+ and Si_{45}^+ were found to be unreactive with ammonia and methanol, whereas Si_{36}^+ and Si_{42}^+ were found to be very reactive. This implies a periodicity of six atoms in the reactivity pattern for clusters ranging from 30 to 45 atoms. For clusters larger than 45 atoms the reactivity appeared to monotonically increase.

J. C. Phillips[2] suggested that silicon forms six-membered rings in a carbon-like fashion and proposed a structure (for Si_{39}) of stacked rings with a three-atom cap. We took this suggestion literally, and in what we believe to be the first calculation which tried to explain this data, proposed a series of stacked benzene rings and attempted to show that this accounted for the experiment.[3]

Subsequent experiments were performed by the same group[4,5] in which clusters ranging from 20 to 60 atoms were photofragmented. They found that the clusters tended to explode into 10 atom fragments, rather than simply losing a few atoms. This effect seems universal over the entire range of clusters. Again, we proposed a structure which purports to account for this data,[6] suggesting stacked naphthalene rings. This also considers silicon and carbon to be chemically similar, and we shall have more to say about the benzene- and naphthalene-derived structures in what follows.

Similarly important experiments[7,8] found no significant reactivity with ammonia over a range of cluster sizes, and further found that the reactivity of all clusters is much smaller than that of the bulk surface. Results with oxygen,[9] water[10] and ethylene[11,12] tend to reinforce the notion of relative inertness. On the other hand, Elkind et al's original results have been reconfirmed.[13] A controversy has now emerged as to what accounts for the apparent contradiction.[7,14,15] Since the experimental evidence is at least ambiguous if not contradictory, it is therefore impossible to account for all of it.

Much theoretical work has been done on the structure of Si_{45} and other mid-sized clusters. We have already mentioned our early efforts at tackling this problem, where we have highlighted the chemical similarity between molecular forms of carbon and silicon, and our structures therefore have relatively little in common with the bulk silicon structure. In a similar vein, silicon in the Buckminsterfullerene form has also been proposed.[16] Other workers have taken the opposite point of view and have suggested that the clusters are just very small micro-crystallites. The best example of this appeared in several papers which assumed cluster atoms arranged along various lattice sites such as fcc and hcp.[17,18]

Perhaps the most ingenious structure was presented by E. Kaxiras.[19,20] He suggested that Si_{45} consists of a single, bulk-like atom surrounded by a reconstructed surface. Kaxiras has shown that this structure is stable under a variety of classical force field potentials, and has done *ab initio* calculations on a similar Si_{33} cluster. His result attempts to explain the relative inertness of Si_{45} by indicating that only "magic" numbers of atoms can be constructed in this form. It has been suggested that this is similar to Buckminsterfullerene in that it consists of 44 atoms (not counting the central atom) arranged in 12 pentagons and 12 hexagons.[9]

In a Comment on Kaxiras' work,[21] we have proposed two additional structures which have complete tetrahedral symmetry. These resemble Kaxiras' in that they all have a tetrahedrally-situated central atom, but are surrounded by what we describe as reconstructed clusters rather than a reconstructed surface. A more detailed account of these isomers will be given later.

Finally, we mention a structure proposed by Patterson and Messmer.[22] They also begin with bulk lattice structures and have suggested an aesthetically pleasing alternative. This also has T_d symmetry, and the authors suggest many reasons why it may be consistent with experiment. These include the relative stability of various isomers, the relatively few number of dangling bonds, and patterns which reflect a six- and ten-atom periodicity.

The major purpose of this paper is to use a tight-binding (TB) model to compare five isomers of Si_{45}. Further, many of these structures contain slight variations, and some of these will be investigated also, leading to approximately 10

isomers of Si_{45}. We will also briefly consider Si_{39} in an attempt to correlate our data with experiment. Finally, two classical force field models will be used as a check on the TB results.

In the next section we describe the TB method in greater detail. In Section III we present our results, and in Section IV we discuss the implications thereof. Brief concluding remarks are contained in Section V.

II. METHOD

The TB model which we use was first developed by Tománek and Schlüter[23,24] and extensively tested by us.[25,26] A complete account of the method is given in those references, along with Refs. 3 and 6. We only briefly summarize here, emphasizing those aspects which are significant for what follows.

We write the TB Hamiltonian as

$$H_{TB} = \sum_{\mu a} \varepsilon_a^0 a_{\mu a}^\dagger a_{\mu a} + \sum_{\mu\alpha\nu b} V_{\mu\alpha,\nu b} a_{\nu a}^\dagger a_{\mu b} \quad , \qquad (1)$$

where $a_{\mu a}^\dagger$ and $a_{\mu a}$ are the electron creation and annihilation operators in the basis $|\mu a\rangle = \phi_a(r - R_\mu)$, with $\phi_a = \{3s, 3p_x, 3p_y, 3p_z\}$ as the valence orbitals of silicon atom at sites μ with coordinates R_μ. The parameters ε_a^0 and $V_{\mu a}$ are empirically fit to the band structure of bulk silicon.[23,26] The band structure energy of the cluster is therefore

$$E_{BS} = \sum_p n_p \varepsilon_p - N \sum_a n_a^0 \varepsilon_a^0 + U \sum_\mu (q_\mu - q_\mu^0)^2 \quad . \qquad (2)$$

The first term is the TB energy, the second represents the energy of the isolated atoms, and the last term represents Coulombic repulsion within the cluster, where the constant U is estimated at 1 eV.

To make the model appropriate for clusters, two additional terms must be added to account for repulsive terms.[23] These are the diatomic repulsion term, $E_d(R_{\mu\nu})$, analytically fit to *ab initio* data, and a term related to the average coordination number of the cluster. These are given by

$$E_R = \sum_{\mu<\nu}^{N} E_d(R_{\mu\nu}) - N\left[c_1\left(\frac{N_b}{N}\right)^2 + c_2\left(\frac{N_b}{N}\right) + c_3\right] \quad , \qquad (3)$$

where N_b is the number of bonds in the cluster, N is the number of atoms, and the c's are fitted to *ab initio* studies of diamond and fcc lattices, along with the potential curve for the silicon dimer. For comparison to classical potentials, it is important to point out that a bond-angle dependence is explicitly included in the TB Hamiltonian through Eq. (1), and implicitly through Eq. (3). This model may be expected to be accurate for coordination numbers less than 8. The cohesion energy of the cluster is then given by .

$$E_{coh} = -(E_{BS} + E_R) \quad . \qquad (4)$$

Apart from $E_d(R_{\mu\nu})$, which is calibrated to *ab initio* results for the dimer, all parameters in this model are derived from calculations with bulk lattices. Thus there is no assurance that the model will apply to clusters. The initial check was performed by Tománek and Schlüter in their original paper, where they compared TB results with a local density approximation, finding qualitative agreement.[23] We have done extensive work comparing the results of this model for Si_{10} with other calculations and with experiment.[26] Our results are in excellent agreement. Recalling that the TB model is a nearest-neighbor model, distinguishing nearest neighbors is an integral part of the procedure. For the bulk this is easy, since nearest neighbors are about 2.4 A apart, and next nearest neighbors are 3.8 A away. Thus the bond margin (the distance between the longest bond and the shortest unbonded pair) is 1.4 A. Thus any bond cutoff distance chosen between these two points will not affect the result, but the midpoint between them is 3.1 A.

For clusters the situation is more ambiguous. In particular, we found the most stable Si_{10} structure to be a Jahn-Teller distortion of the bicapped tetragonal antiprism. This results in two atoms slightly less than 3.3 A apart. Whether or not these two atoms are considered to be bonded was decided by comparison with experiment.[27] The calculated HOMO-LUMO gap matched that from experiment exactly if we chose the cutoff at 3.3 A, thus including the long bond. We can therefore

consider the cutoff parameter to be experimentally derived for small clusters. Since we have good reason for accepting the 3.3 A cutoff for small clusters, we are reluctant to abandon it for larger. On the other hand, the appropriate cutoff in the bulk is the midpoint of the bond margin, or about 3.1 A, and one could argue that larger clusters are more bulk-like. In the case of Si_{10}, the relevant experimental data was the HOMO-LUMO gap, but the dipole moment of the cluster, or any other measurement which gives some information about the electronic structure, will specify the cutoff distance. For Si_{45} we have as yet no such experimental data, and so we shall present our results using both 3.1 A and 3.3 A cutoff distances, along with potentially measurable consequences of each choice. The advantage of this approach is that the parameter has definite physical significance, but we shall see that it affects only the details of the geometry and energy of the clusters. In most cases the cutoff value makes no difference at all, since either cutoff distance lies squarely within the bond margin. But when significant, it changes the topology of the molecule, and therefore has a large effect on the electronic properties.

For each of the clusters studied, we performed a global geometrical optimization using the TB model. This was done initially by using Hellmann-Feynman forces for a rapid approach to equilibrium, followed by at least 1800 variational steps. The advantages of this approach are several-fold. Unlike classical potentials, the TB model gives us information about the electronic structure of the cluster, data which shall prove very useful in what follows. And unlike *ab initio* techniques for clusters of this size, no symmetry constraints are imposed on the calculation, and hence subtle effects such as Jahn-Teller distortions can be explicitly discussed.

We have also checked our results against two classical potentials, proposed by Kaxiras and Pandey (KP)[28] and Tersoff (T).[29] The KP potential was designed to mimic distorted tetrahedral geometries and is clearly appropriate for Kaxiras' proposed geometry for Si_{45}. It is less appropriate for other geometries, as shall be described later. The T potential resembles the TB model in that it contains a relatively well-defined cutoff distance and bond order. Thus the three-body term is contained within the bond-order term, under the assumption that a highly-coordinated

atom is less strongly bound to any given nearest neighbor. Hence this potential could be expected to be more accurate for more highly-coordinated species. Neither potential was designed explicitly for clusters, and given the lack of experimental data from which to fit such a potential, this is not surprising.

II. RESULTS

We have performed calculations on six basic structures for Si_{45}. Four of these have been previously described in the literature, and two are presented here for the first time. The results are summarized in Table I. We consider each case individually.

The benzene structure (abbreviated BENZ, shown in Fig. 1) was first proposed by our laboratory.[3] The attempt was to explain the periodic reactivity described above,[1] and also to accomodate the behavior of silicon. We supposed that silicon would prefer to be tetra-coordinated, and that the cluster would rearrange by straining the bond angles rather than through higher coordination numbers. Only the three-atom cap was more highly coordinated. The structure is close to C_3 symmetry and has a modest band gap and bond margin. The cohesion energy is not the highest of all structures considered. Nevertheless, in light of subsequent data, we no longer consider it a plausible candidate.

The naphthalene structure (abbreviated NAPH, shown in Fig. 2) was an attempt by our laboratory[6] to describe the 10-atom photofragmentation phenomena.[4,5] Again, we supposed that silicon would form small graphitic plates analogous to carbon, with dangling bonds accommodated by bonding the plates together. We indicated that the cluster could then photofragment into 10-atom pieces. We also predicted that the cluster would assume a bulk-like geometry beginning at 65 or 78 atoms, at which point interior atoms would occur. We still believe that the NAPH structure accounts for the photofragmentation data better than any other proposed structure, but it similarly fails to account for most other data. The photofragmentation effect appears universal across the entire spectrum of silicon clusters, from 20 atoms and larger, that any model to describe it must either be independent of the geometry of the parent cluster, or suppose some consistent geometry such as the NAPH structure. The previous paper was based on the latter premise, but we are increasingly drawn toward the former. It seems improbable that clusters of such a wide size range

would have similar geometries and yet be dramatically different in other respects. We therefore come reluctantly to the conclusion that the photofragmentation data yields little or no information about the structure of the parent ion.

The ideal NAPH structure has a single mirror plane, though our global optimization distorts even that. There seems to be no symmetry at all. The HOMO-LUMO gap is respectable, though not large, and the bond margin is small, indicating that the structure is very sensitive to the cutoff value. We have performed the calculation using only 3.3 A. More interesting is the LUMO level, which is very high. It may be supposed that the structure with the largest LUMO level would be less reactive than clusters with low-lying LUMO levels, and this would indicate low reactivity for this species. However, the small band-gap tends to counter this trend. The cohesion energy is slightly higher than average. Similar to BENZ, we no longer consider it to be a viable candidate.

The third structure was presented by Kaxiras[19,20] (abbreviated KAX, shown in Fig. 3). It consists of a bulk-like atom surrounded by a reconstructed solid surface. This structure has the lowest average coordination number of any structure here considered, with no atom more than tetra-coordinated, and most atoms only triply coordinated. Further, the lowest coordination numbers are contained on the outside of the structure, indicating a large number of dangling bonds, and indicating also a highly reactive species. This assessment is confirmed by the data. The calculation listed as KAX sym. is a TB calculation on the original Kaxiras coordinates, unoptimized in the TB model. We include this to show that the ground state is degenerate. Since a degenerate ground state depends on the symmetry and topology of the structure, and therefore on the cutoff distance, we note that the bond margin is well defined, and thus any shorter cutoff value (i.e., more bulk-like) is not going to change this result.

We have also performed a global optimization of the KAX structure. This must be considered a Jahn-Teller distortion of the original structure. Of course the cohesion energy is lower, but still higher than that observed for BENZ and NAPH. The band-gap is now 0.044 eV, which is the lowest of all non-degenerate species, and the LUMO level is also relatively low. These results reconfirm the chemist's intuition that this would be a very reactive species, and we think it is an

improbable solution to the Si_{45} problem. It is worth pointing out that this structure is closest to bulk-like of any tried, and therefore the TB model can be expected to be most accurate.

The fourth structure was proposed by Patterson and Messmer[22] (abbreviated PM, shown in Fig. 4). It is an O_h species with an average coordination number of 3.4. Again, the lowest coordination numbers are located at the outside of the cluster, indicating a large number of dangling bonds, as noted by the original authors. Thus we see that the unoptimized structure (PM sym.) has a degenerate ground state. The optimized structure, which must also be a Jahn-Teller distortion, has a relatively low cohesion energy, a small band gap, and a 0.083 eV LUMO level. All of this implies that the isomer is reactive and therefore not the probable Si_{45} isomer. Further, the bond margin is stable, indicating that the structure is meta-stable, and that the optimized structure, while distorted, does not differ dramatically from the unoptimized model used as input.

Finally, we consider the two new isomers proposed in this article. These were discovered serendipitously in attempting to reproduce Kaxiras' results using classical potentials.[21] Both have full T_d symmetry and are abbreviated as T1 and T2 in Table 1. The T1 structure is shown in Fig. 5 and Table II, and the T2 structure in Fig. 6.

The structures may be described as follows. T1 and T2 both have a central atom, denoted 0, tetrahedrally-coordinated (except as described below) to atoms I, similar to KAX. In addition to the 0 atom, the four atoms I are each bonded to three atoms II (there are 12 of these). Atoms II share a bond with atom I, with another atom II, and with two atoms III. Atoms III, each tetra-coordinated, form a six-membered ring at the surface of the cluster. The bonds between atoms I, II and III form alternately four- and five-membered rings. Finally, the hexagons are capped by an atom IV, which is hexa-coordinated to each member of the ring. There is 1 atom 0, 4 atoms I, 12 atoms II, 24 atoms III and 4 atoms IV. T2 differs from T1 only in that the caps become pockets, inserted through the ring.

The average coordination number for T1 is 4.2. All atoms are tetra-coordinated except for the cap atoms. The cap atoms, at the surface of the cluster, are most coordinated indicating that they will be least reactive, so insofar as Si_{45} is an unreactive species, this isomer then qualifies. The cohesion energy for both

T1 and T2 is lower than for any other isomer. While the HOMO-LUMO gap for T2 requires further discussion below, for T1 it is as large as any of the isomers listed at 0.256 eV. For T1 the bond margin is such that varying the bond cutoff between 3.1 A and 3.3 A has no effect. While we previously reported that T1 was unstable under the TB model,[21] we have subsequently found a metastable isomer, though the activation energy to T2 is very low.

III. DISCUSSION

The precise energy of a cluster is difficult to measure, as the debate over whether or not clusters are properly annealed indicates.[7,14] It is possible that a variety of isomers exist in a given experiment, and we see from Table 1 that T1 and T2 differ by barely a tenth of an eV. If other related isomers exist which are closer in energy, it may not be possible to isolate a single structure by annealing. Thus it could be impossible to resolve the structure(s) of Si_{45} by simple energy calculations, and other experimental data will be required. These are reactivity data,[1,7-15] electrical and optical data[25,27] and photofragmentation data.[4,5]

We turn first to the reactivity data. The group at Rice University has reported a variation in the reactivity of silicon clusters with a variety of reagents.[1,9,12] We have pointed out that these are mostly nucleophiles (NH_3, CH_3OH),[3] while little variation was found with other reagents (free radicals such as oxygen, nitrogen oxides). This group has found that Si_{33}^+, Si_{39}^+ and, especially, Si_{45}^+ are particularly unreactive. The reaction appears to be chemisorption, sometimes of multiple molecules, and it is unclear whether or not it is dissociative chemisorption as occurs on a bulk surface. Another group at Bell Laboratories disputes these findings and suggests that all clusters are equally reactive, with none reacting in a manner similar to a bulk surface.[7,8,10,11,13]

It first must be stated that the reactivity pattern has little to do with cluster stability. The former is a kinetic effect, whereas the latter is thermodynamic. There seems no reason to suppose that Si_{45}^+ is qualitatively more stable than Si_{44}^+ or Si_{46}^+, except that larger clusters are more stable than smaller ones. The experimental evidence does not show any consistent variation in the abundance of clusters as a function of size, and also no spontaneous dissociation of larger clusters into smaller ones has been reported. Therefore, it is improbable

that energy calculations are going to determine the reason for the relative inertness. Briefly, stability and reactivity may be completely separate issues, a distinction which is frequently lost in the literature.[16,17,22,30]

The reasons for a variation in reactivity may be severalfold. First, there could be a charge distribution across the molecule.[3] Given the nucleophilic nature of the reagents and also the relative inertness of the negatively-charged clusters, this possibility cannot be excluded. Clusters in which the charge is evenly dispersed will tend to be less reactive than those where the charge is concentrated. This would tend to favor symmetrical species where the HOMO orbital spans the entire molecule.

A second cause of increased reactivity is the electronic structure of the cluster. An open-shell cluster may be expected to be much more reactive than the closed-shell species. Here it is important to point out that the experiments are performed with ions rather than with neutral clusters, and all singly-charged ions will be open shell, in essence, free radicals. Therefore, it is not surprising that they react quickly with other radical species. But the variation in reactivity indicates that this can't be the only cause, and therefore we suggest that the electronic structure of the neutral species (which we have calculated) is relevant. In particular, a nucleophile such as ammonia, with two electrons to contribute, will react quickly with an empty, low-lying orbital, as is found in the open-shell species. Similarly, a comparison of LUMO levels is instructive. If the LUMO is low in energy, then the cluster may be considered more reactive than otherwise.

Thirdly, the coordination number may be considered a clue to reactivity. Clusters with low coordination numbers at their surface can be expected to be more reactive than their counterparts with high coordination numbers, where dangling bonds are minimized. Obviously, insofar as double bonds or conjugated systems occur, this rule does not hold but there is little indication that double bonds or conjugated phenomena are a major factor with silicon. First is the dramatic difference in the chemical behavior between silicon and carbon, and second is the close similarity between silicon and germanium clusters. All this indicates that silicon tends to be sp^3 hybridized, and highly-conjugated systems such as appearing in Buckminsterfullerene are not to be expected.

Finally, strain energy may be a source of reactivity. Highly-strained bond angles will be more reactive than less strained species, and clusters which retain tetrahedral angles will probably be less reactive than their counterparts. Clearly, very small clusters must have high strain energies, and for similar reasons, the surfaces of large clusters must also be strained.

With respect to the optical and electronic properties of clusters, we have used the TB model to predict the spectra and (hyper)polarizabilities of Si_{10}. These are a very sensitive measure of the structure of the cluster. For Si_{45}, however, this calculation becomes prohibitively complex, and so we are limited to the simplest calculations. These are the HOMO-LUMO gap and the dipole moment. The symmetry of a molecule determines both. In general, a Jahn-Teller distorted species will have a dipole moment, whereas the undistorted cluster will not. While other possibilities are imaginable, we suggest that if a dipole moment is measured in Si_{45} it is probably due to a Jahn-Teller distortion of one of the tetrahedral or KAX structures.

We now consider the relative advantages of the TB model in probing each of the above effects, beginning with charge distribution. As long as the separation of charge is small, the TB model is probably qualitatively accurate, but for large charge separations and/or ionic species, the present TB method may not be valid. At the present time, however, we use the charge distribution data in only the most qualitative way: to distinguish a molecule with a dipole moment and as a test of symmetry.

The electronic structure of the cluster, on the other hand, is probably given fairly accurately by the TB model, at least near the HOMO level. This is because the original parameters have been fitted to the band structure of bulk silicon, and also because we have reproduced the HOMO-LUMO gap for Si_{10}. The study of Si_{10} optical data provides a wealth of material against which the TB model can be tested and refined. In our opinion, this is the one great strength of the present method: it gives some information about excited states without arduous calculation. Determination of open- and closed-shell species depends primarily on the accuracy of the relative energies of orbitals near the HOMO level, and the TB model can be expected to be most accurate there, by virtue of fitting. This is especially true

in larger clusters which are bulk-like in structure. Allen, Broughton and McMahon[31] have developed another TB fitting for bulk silicon and which is probably superior in the treatment of excited states, but which has not yet been extended for use in cluster calculations.

Strain energy is accounted for in two ways. First, the angular dependence of the original atomic orbitals is explicitly built into the model. Secondly, strain depends on the coordination number. This has been fitted to various *ab initio* lattices, as discussed above. Therefore, especially for clusters which are bulk-like and have coordination numbers of 8 or less, the present TB model is sufficient. This is borne out by Tomånek and Schlüter's original comparison with the local density approximation (LDA) results with small clusters, and by our results for Si_{10}.

All of the above clusters are stable under the classical potentials listed above, with the exception of T1 and T2.[21] The KP potential shows T1 to be the preferred structure, whereas the Tersoff method indicates T2. This is consistent with the stated aims of the potentials, in that T2 may in some ways be considered to have a larger coordination number, and in any event, the angles are far from tetrahedral. Therefore, one would expect that the Tersoff potential would find it more favorable. The KP potential, on the other hand, gives a greater weight to tetrahedral symmetry, and in T1 the tetrahedral angles are preserved to the greatest extent possible. We finally note that the cutoff distance in the KP potential is 5.5 A, a distance which includes second-nearest neighbors in the bulk lattice. Thus it is very difficult to assign bonds within the KP model, and the coordination number is therefore undetermined. Simply stating that only nearest neighbors are bonded is ambiguous in the case of clusters. The Tersoff model includes a continuous cutoff function decaying over 0.2 A and including first-nearest neighbors.

As previously stated, the TB model also indicates that T2 is the preferred structure, being lower in energy by about 0.1 eV. We now consider more closely the differences between T1 and T2. If the bond cutoff is defined at 3.1 A, then T1 and T2 are topologically identical, and the difference in cohesion energy is due solely to geometry, i.e., bond angles. Both T1 and T2 (with a 3.1 A cutoff) are 94 bond

systems, with an average coordination number of 4.2. In both cases, all atoms are tetra-coordinated except for the four cap atoms. As is clear from Table I, the HOMO-LUMO transition and the dipole moment are well-defined by the symmetry and are approximately the same for both systems.

If the bond cutoff distance is changed to 3.3 A, then the situation is quite different. In this case the cap atoms in T2 are loosely bonded to the central atom, making it octa-coordinated and yielding a 98-bond structure. The most dramatic difference, however, is that the 98-bond isomer is degenerate, and therefore must be Jahn-Teller distorted. Global relaxation of the species yields a 96-bond structure in which two cap atoms are bonded to the central atom and two are not. It must be pointed out that the geometric distortion is small, the bond margin is small, and the primary difference is one of topology rather than geometry, and therefore is very sensitive to the cutoff parameter. The 96-bond isomer, which is the lowest energy configuration of any Si_{45} isomer, has a HOMO-LUMO gap about equal to the 94 bond isomer (T1), and unlike other isomers, it has a dipole moment.

The true value of the bond cutoff parameter must be determined from experiment, and at this point we have no data with which to make such a determination. Our best guess is that a value of 3.1 A is better since it preserves the largest bond margin, and thus retains the physical significance of the cutoff value. It is also the midpoint between nearest and next-nearest neighbors in the bulk, and insofar as Si_{45} is bulk-like, then this bulk property could be expected to apply. A 3.1 A cutoff implies the bulk-like property of lower coordination numbers. The 94- and 98-bond versions of T2 can be experimentally differentiated by observation of the HOMO-LUMO distance. The 96-bond version can be distinguished by looking at the dipole moment. Thus we conclude that the cutoff distance is ultimately amenable to experimental determination.

Many authors, including Tersoff[29] and Khan and Broughton,[32] have suggested that a continuous function be used for the cutoff. In principle this is a very good idea, but it introduces another parameter into the model. Given the present lack of experimental data, it is doubtful that two parameters could be better fitted than one. Further, the simpler model yields a clearer physical insight into the system, as the previous discussion of coordination numbers indicates.

We now consider the reactivity pattern in units of six atoms. In order to generate a fully tetrahedral structure, one requires 4n + 1 atoms. Thus 33 and 45 atoms qualify, but it is impossible to generate a structure with tetrahedral symmetry from Si_{39}. Therefore, tetrahedral symmetry alone does not seem to assure low reactivity, though it would seem to contribute to that effect. The other obvious feature of T1 and T2 are the capped hexagonal rings. It thus seems reasonable to suppose that Si_{39} would consist of an Si_{45} cluster *sans* one ring. This is most probable in the T2 case since the cap atom becomes a real cap, stabilizing the remainder of the structure. Thus Si_{39} assumes a trigonal pyramid geometry with C_3 symmetry.

To investigate this possibility closer, we used the TB model to find a metastable isomer of Si_{39} beginning from the T2 geometry without one ring. A structure was found in which the atoms II surrounding the empty site formed another ring, which was then topped by the remaining cap atom. This structure had a cohesion energy of 3.88 eV and a dipole moment of 2.45 D. We have made no global study of Si_{39}, and there are undoubtedly many other possible configurations, but this indicates that this model is plausible. All the reasons for low reactivity for Si_{45} apply to Si_{39} as well, except that the cohesion energy is somewhat higher, as expected for the smaller cluster.

The photofragmentation into 10-atom pieces is nearly universal, ranging over all sizes of clusters from 20 atoms up, and also for germanium clusters. Perhaps all such clusters are built up of 10-atom fragments, but this seems unlikely, especially for larger clusters. The probable Si_{10} cluster is molecular in structure, with an average coordination number of 5 and no atom with anything resembling tetrahedral symmetry. All of the proposed Si_{45} structures have coordination numbers closer to 4, and in the case of KAX, less than 4. The most likely candidates assume tetrahedral symmetry around the central atom, and strained tetrahedra around other atoms, i.e., a more bulk-like geometry. Thus if the 10-atom cluster is "built in" to larger species, it contradicts all other evidence.

It is possible to devise fragmentation patterns for each of the clusters listed, and the inspiration for the NAPH structure is precisely to account for the fragmentation pattern. Kaxiras[19] also mentions that the KAX structure can lose 10

atoms in such a way as to weaken the entire structure. But this will almost always be true for any isomer, since it is known that the cohesion energy per atom increases monotonically with the number of atoms. Therefore, any smaller cluster will have a lower cohesion energy, which constitutes no evidence for the fragmentation pattern. We can make a similar argument for T1 and T2 by noting that the hexagonal ring plus cap contains 7 atoms, and then including three of the six atoms II bonded to each hexagon (which three remains uncertain) will produce a 10-atom cluster, of which there are four along with a five-atom remnant consisting of atoms 0 and I. In some sense, the T1 structure is a more likely candidate for this argument since it is bulk-like at the center, and molecular (highly coordinated, strained angles) at the edge, and can thus be considered a bulk fragment surrounded by clusters.

The above paragraphs may provide a clue to the photofragmentation data. Very small clusters (three or four atoms) are too small to have large coordination numbers, and therefore are very reactive. Thus it may be that large clusters are broken apart into small pieces, but that these rapidly react with each other to form the highly-coordinated Si_{10} species. It is not, therefore, that Si_{10} is exceptionally stable (or that 10-atom fragments are hidden in every cluster), but rather that it is relatively unreactive.

The optical spectrum of Si_{10} also offers a clue about the photofragmentation pattern. Cheshnovsky et al[27] report that while Si_{10} has a well-defined HOMO-LUMO gap (1.2 eV), Si_8, Si_9 and Si_{12} appear to be degenerate, and Si_{11} nearly so. If a degenerate ground state is more reactive than a non-degenerate one, then a reason for the relative inertness of Si_{10} is apparent, and therefore when photofragmented clusters recombine, a 10-atom fragment is a probable product over the time scale of the experiment. However, no conclusions about the thermodynamic stability of Si_{10} follow from this argument.

We conclude that the photofragmentation spectra tells us little about the structure of the parent ion. Since the spectra are so much alike, it is a property that all ions have in common, and except for NAPH, none of the listed structures can properly account for it. We suggest that the photofragmentation spectra have more to do with the photofragmentation process than with the parent ion. A possible

mechanism is the breakup of the molecule into many small pieces which then recombine into 10-atom clusters, and hence all data about the structure of the parent is lost.

V. CONCLUSION

We conclude with the statement that a 94-bond structure similar to T1 or T2 is the probable structure for Si_{45} (an experimental resolution between these would be difficult). The salient arguments are: 1) The structures are lowest in energy under both the TB and two classical models. 2) The structures are similar to the bulk (except for the caps) in that they are entirely tetra-coordinated. Seventeen atoms are located in nearly exact tetrahedral centers, 24 atoms (the rings) are strained tetrahedra (less strained in the case of T1), and the cap atoms are hexa-coordinated. 3) The structures are more highly coordinated at the surface than at the center. This will tend to make them less reactive. 4) The structures have well-defined HOMO-LUMO gaps, also minimizing reactivity, corresponding to some of the experimental evidence.[1,4,5,9,12] 5) Strain energies are relatively low, and where high, are counteracted by high coordination numbers, thereby stabilizing the atom.

We favor the results in which the bulk-like bonding topology is preserved, and this implies the 3.1 A cutoff distance. The experimental evidence for a definitive resolution of the cutoff value does not yet exist. If Si_{45} is more bulk-like than smaller clusters, which by all accounts it appears to be, then the TB model should be more appropriate. We are therefore most confident with our results for KAX, and somewhat less so for the other structures. The structures for which the bond margin is small are obviously less reliable. However, for the 3.1 A cutoff both T1 and T2 are stable, of lowest energy and physically reasonable.

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REFERENCES

1. J. L. Elkind, J. M. Alford, F. D. Weiss, R. T. Laaksonen and R. E. Smalley, J. Chem. Phys. 87, 2397 (1987).
2. J. C. Phillips, J. Chem. Phys. 88, 2090 (1988).
3. D. A. Jelski, Z. C. Wu and T. F. George, Chem. Phys. Lett. 150, 447 (1988).
4. Y. Liu, Q. -L. Zhang, F. K. Tittel, R. F. Curl and R. E. Smalley, J. Chem. Phys. 85, 7434 (1986).
5. Q -L. Zhang, Y. Liu, R. F. Curl, F. K. Tittel and R. E. Smalley, J. Chem. Phys. 88, 1670 (1988).
6. Z. C. Wu, D. A. Jelski and T. F. George, J. Clust. Sci. 1, 143 (1990).
7. M. F. Jarrold, Y. Ijira and U. Ray, J. Chem. Phys. 94, 3607 (1991).
8. U. Ray and M. F. Jarrold, J. Chem. Phys. 93, 5709 (1990).
9. J. M. Alford, R. T. Laaksonen and R. E. Smalley, J. Chem. Phys. 94, 2618 (1991).
10. M. F. Jarrold, U. Ray and K. M. Creegan, J. Chem. Phys. 93, 224 (1990).
11. U. Ray and M. F. Jarrold, J. Chem. Phys. 94, 2631 (1991).
12. L. R. Anderson, S. Maruyama and R. E. Smalley, Chem. Phys. Lett., preprint.
13. M. F. Jarrold, J. E. Bower and K. M. Creegar. J. Chem. Phys. 90, 3615 (1989).
14. S. Maruyama, L. R. Anderson and R. E. Smalley, J. Chem Phys., 93, 5349 (1990).
15. For a good review of much of the literature see M. F. Jarrold, Science 252, 1085 (1991).
16. F. S. Khan and J. Q. Broughton, Invited Paper to the 4th International Conference on Supercomputing, Santa Clara, CA, 1989.
17. H. Kupka and K. Jug, Chem. Phys. 130, 23 (1989).
18. H. J. Nolte and K. Jug, J. Chem. Phys. 93, 2584 (1990).
19. E. Kaxiras, Phys. Rev. Lett. 64, 551 (1990).
20. E. Kaxiras, Chem. Phys. Lett. 163, 323 (1989).
21. B. L. Swift, D. A. Jelski, D. E. Higgs, T. T. Rantala and T. F. George, Phys. Rev. Lett. 66, 2686 (1991).
22. C. H. Patterson and R. P. Messmer, Phys. Rev. B. 42, 7530 (1990).
23. D. Tomanek and M.A. Schlüter, Phys. Rev. B 36, 1208 (1987).

24. D. J. Chadi, Phys. Rev. B 29, 785 (1984).

25. T. T. Rantala, M. I. Stockman, D. A. Jelski and T. F. George, J. Chem. Phys. 93, 7427 (1990).

26. T. T. Rantala, D. A. Jelski and T. F. George, J. Clust. Sci. 1, 189 (1990).

27. O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu and R. E. Smalley, Chem. Phys. Lett. 138, 119 (1987).

28. E. Kaxiras and K. C. Pandey, Phys. Rev. B, 38, 12736 (1988).

29. J. Tersoff, Phys. Rev. B. 37, 6991 (1988).

30. E. Kaxiras, Phys. Rev. Lett. 66, 2687 (1991).

31. P.B. Allen, J. Q. Broughton and A. K. McMahan, Phys. Rev. B 34, 859 (1986).

32. F. S. Khan and J. Q. Broughton, Phys. Rev. B 39, 3688 (1989).

TABLE CAPTION

Table I. Data from different clusters. The abbreviations *sym* and *asym* refer to symmetry constrained and unconstrained calculations, respectively. The symmetrical forms of the KAX and PM structures are not optimized under the TB model, and the energies represent those of the input coordinates. T1 and T2 were optimized under the TB model in both symmetrical and asymmetrical forms. Global optimization yields the topologically identical asymmetrical isomers. Structure abbreviations are given in the text. The energy is the cohesion energy of the cluster, relative to 45 isolated atoms. The bandgap is the HOMO-LUMO gap. The LUMO level is the energy of the first excited state; in the case where the bandgap is zero it is also the HOMO level. The cutoff distance is the parameter used in the TB model, as described in the text, and the LongBond is the largest distance between two bonded atoms. The margin is the difference between the longest bond and the shortest nonbonded pair of atoms. The Energy, Bandgap and LUMO values are given in eV. The Cutoff, Margin and LongBond values are given in Angstroms. The number of bonds is unitless, and the dipole moment is given in Debyes.

Table II. The coordinates of the T1 structure optimized under the TB model while retaining T_d symmetry. The cohesion energy of this structure is 3.8423 eV. Units are Angstroms.

FIGURE CAPTIONS

Fig. 1 Structure of Si_{45} consisting of stacked benzene-like rings (BENZ).

Fig. 2 Structure of Si_{45} consisting of stacked naphthalene-like rings (NAPTH).

Fig. 3 Structure of Si_{45} as proposed in Refs. 19 and 20 (KAX).

Fig. 4 Structure of Si_{45} as proposed in Ref. 22 (PM).

Fig. 5 First tetrahedral structure proposed in Ref. 21 (T1).

Fig. 6 Second tetrahedral structure proposed in Ref. 21 (T2).

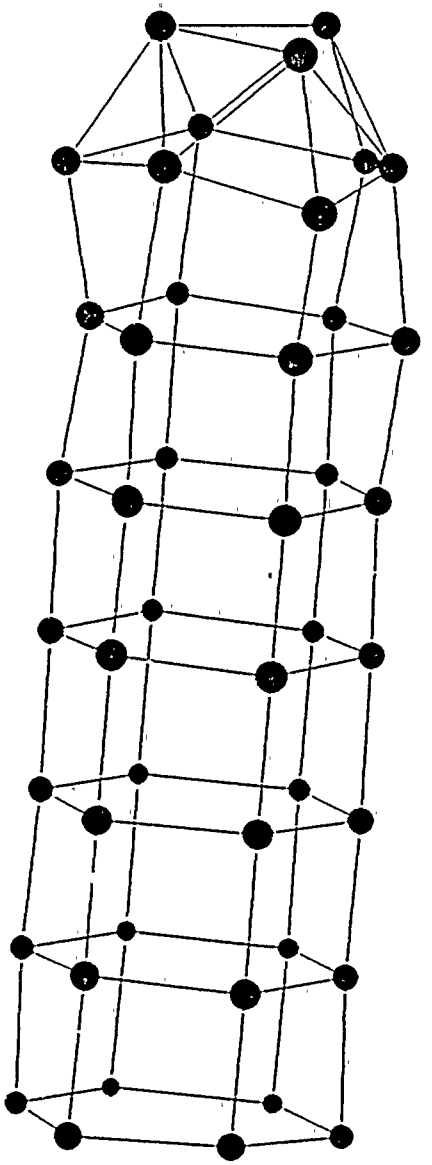
TABLE I

Structure	Energy	Bandgap	LUMO	Cutoff	Margin	LongBond	#bonds
BENZ	3.5548	0.060	0.117	3.1	0.54		90
KAX asym	3.4213	0.044	0.051	3.3	0.84		70
KAX sym	3.0375	0.000	0.148	3.3	0.61	2.39	70
NAPTH	3.6391	0.072	0.159	3.3	0.04		99
PM asym	3.6488	0.037	-0.044	3.3	0.95	2.46	76
PM sym	2.9800	0.000	0.083	3.3	1.07	3.01	76
T1 sym	3.8423	0.256	0.121	3.3	0.83	2.68	94
T2 asym	3.9874	0.103	0.118	3.3	0.00	3.30	96
T2 asym	3.9779	0.126	0.153	3.1	0.62	2.72	94
T2 sym	3.9583	0.194	-0.015	3.1	0.48	2.78	94
T2 sym	3.9765	0.000	0.179	3.3	0.12	3.26	98
SI39	3.8765	0.146	0.121	3.3	0.00	3.30	87

TABLE II

x	y	z	x	y	z
0.000	0.000	0.000	2.569	-4.377	0.712
1.363	-1.363	-1.363	4.377	2.569	-0.712
1.363	1.363	1.363	-4.377	0.712	2.569
-1.363	1.363	-1.363	-0.712	-4.377	-2.569
-1.363	-1.363	1.363	4.377	-0.712	2.569
-2.943	2.943	2.943	0.712	4.377	-2.569
-2.943	-2.943	-2.943	-0.712	2.569	4.377
2.943	-2.943	2.943	-2.569	-0.712	-4.377
2.943	2.943	-2.943	0.712	-2.569	4.377
0.847	-0.847	-3.585	2.569	0.712	-4.377
0.847	0.847	3.585	-4.377	2.569	0.712
-0.847	0.847	-3.585	-2.569	-4.377	-0.712
-0.847	-0.847	3.585	4.377	-2.569	0.712
0.847	-3.585	-0.847	2.569	4.377	-0.712
3.585	0.847	0.847	-2.569	0.712	4.377
-0.847	3.585	-0.847	-0.712	-2.569	-4.377
-3.585	-0.847	0.847	2.569	-0.712	4.377
3.585	-0.847	-0.847	0.712	2.569	-4.377
0.847	3.585	0.847	-0.712	4.377	2.569
-3.585	0.847	-0.847	-4.377	-0.712	-2.569
-0.847	-3.585	0.847	0.712	-4.377	2.569
-2.569	4.377	0.712	4.377	0.712	-2.569
-4.377	-2.569	-0.712			

Fig 1



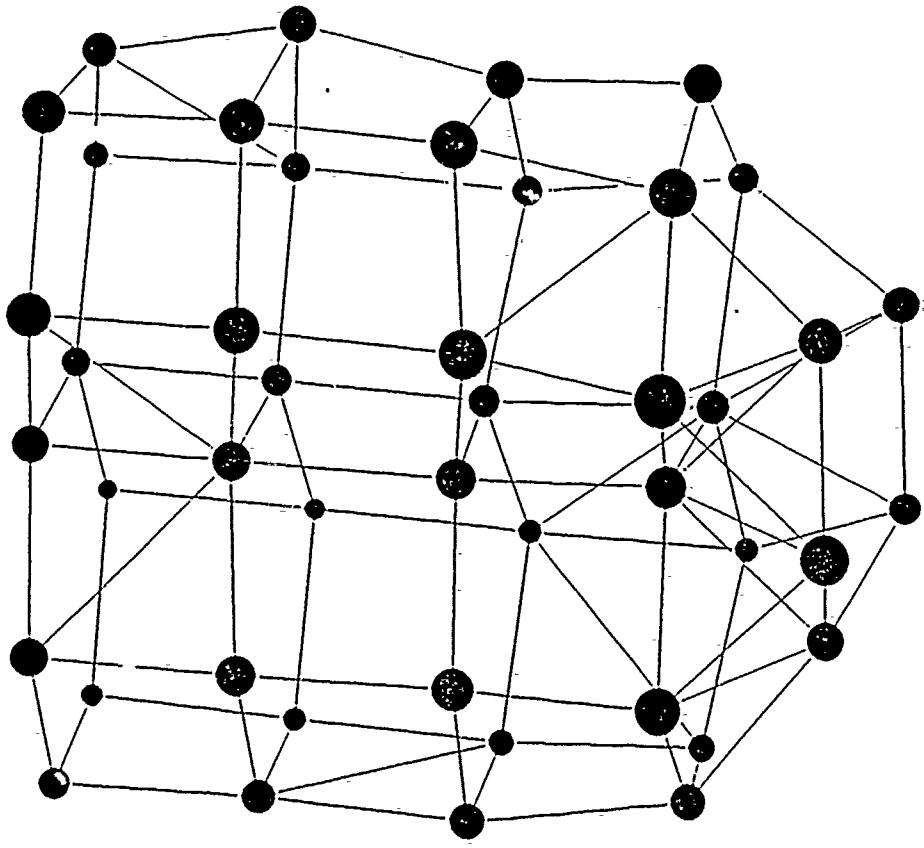


Fig. 2

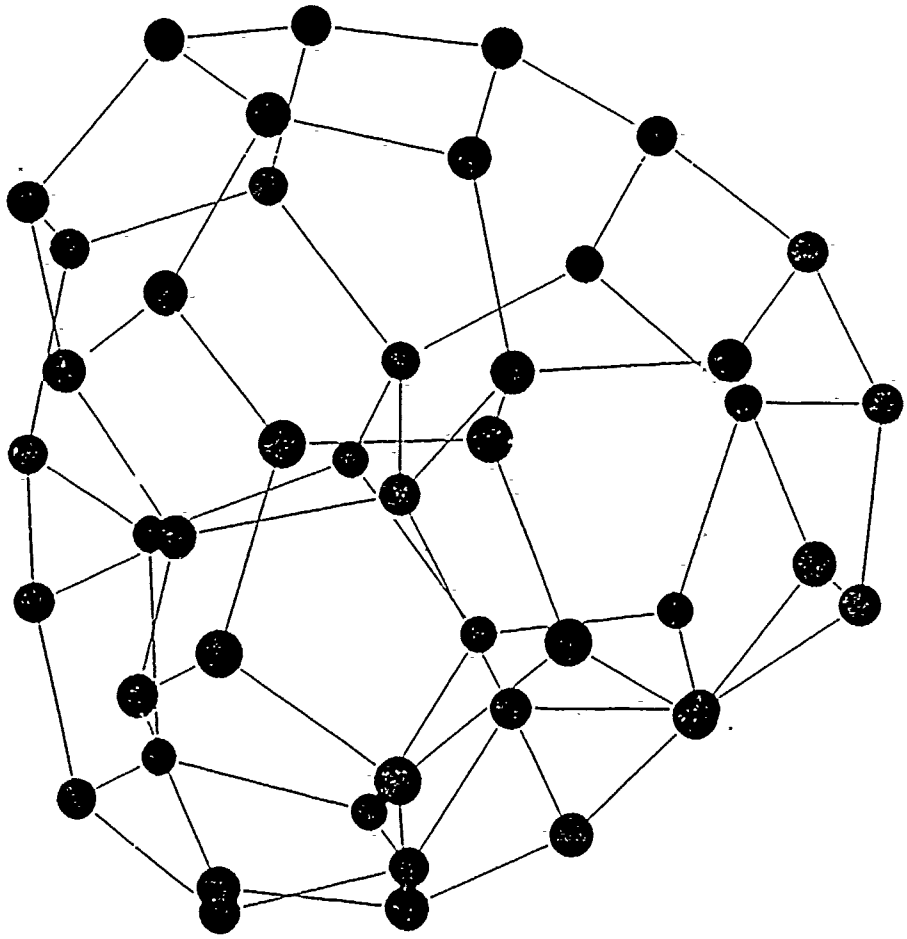
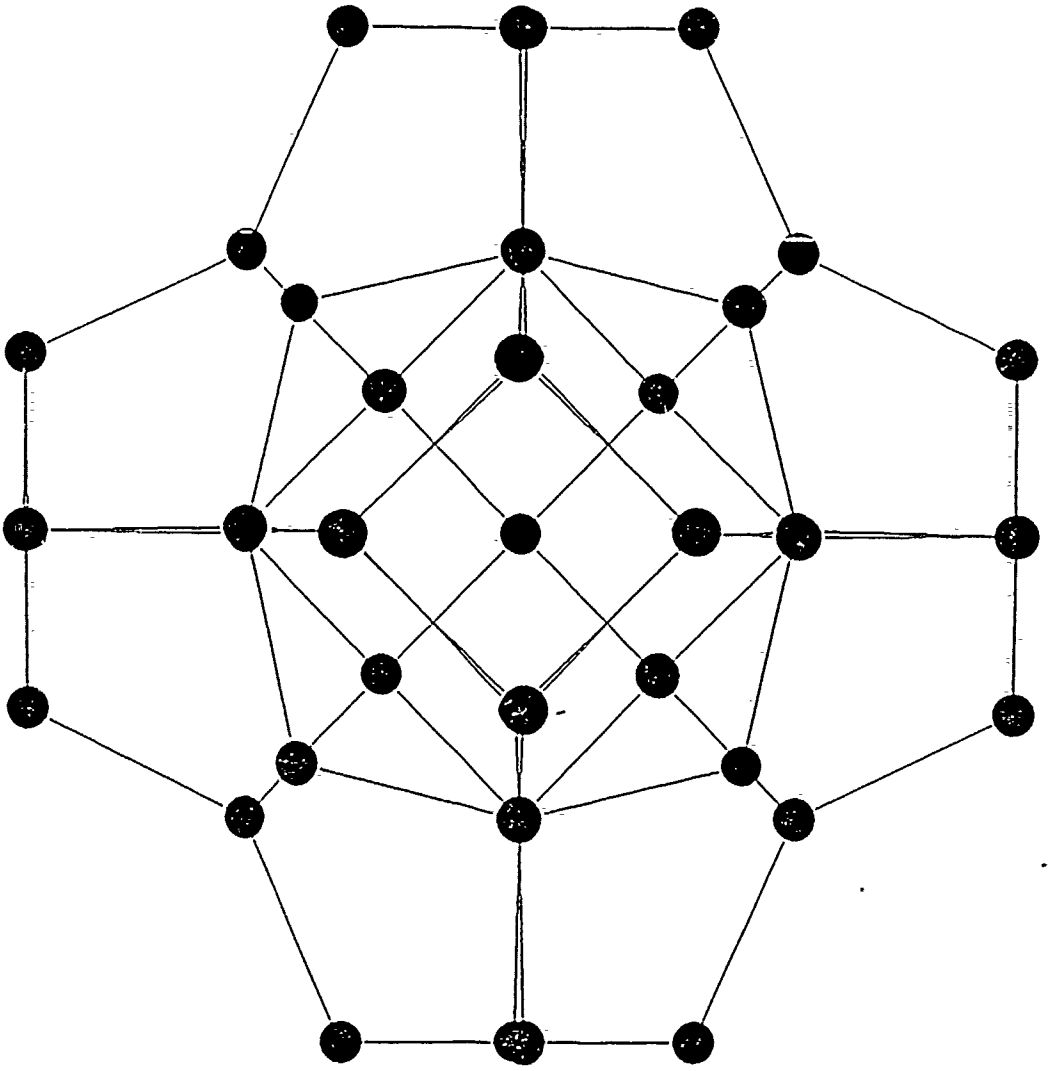


Fig 3



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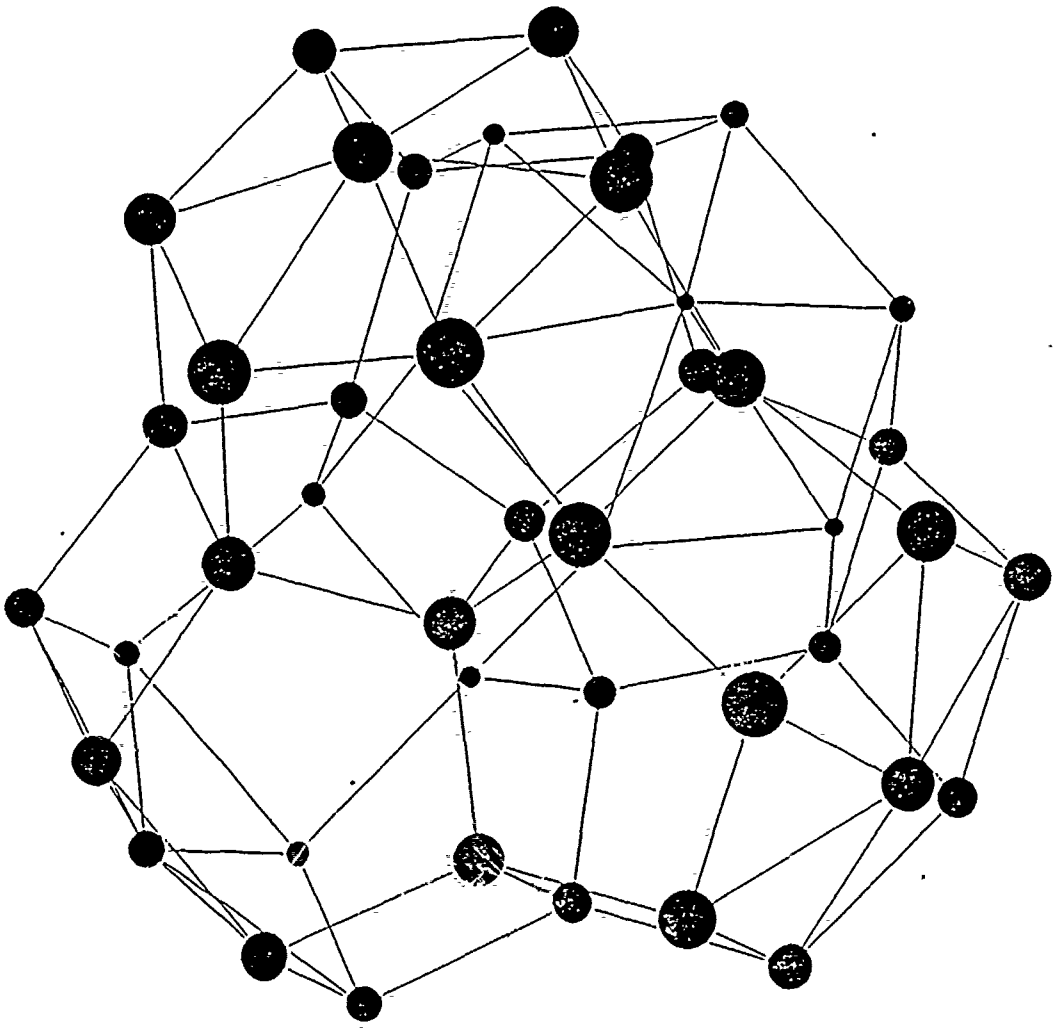

Fig. 5

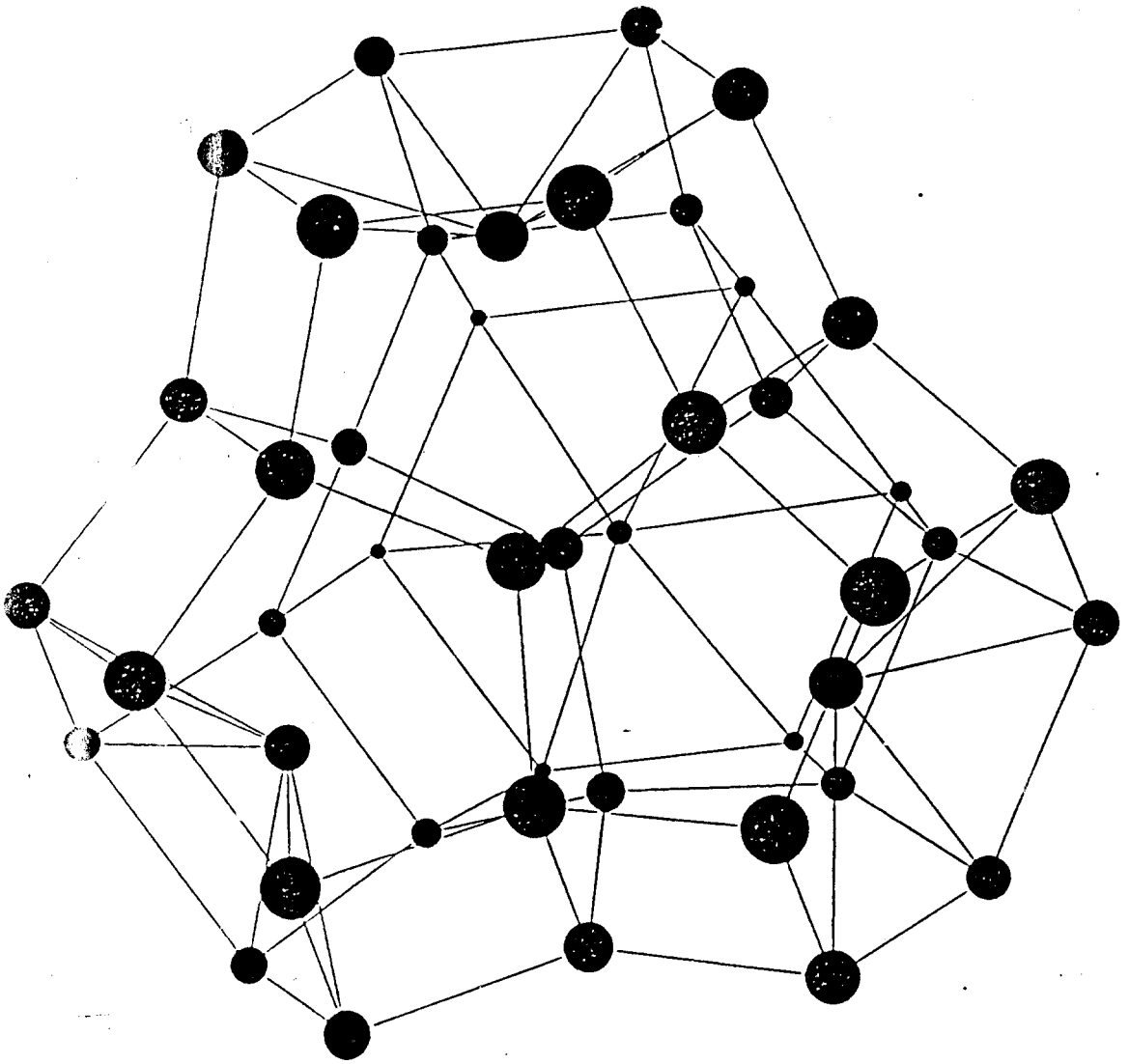

Fig 6